The Quantum Rotations of Confined Methyl Iodide

Robert M. Dimeo

NIST Center for Neutron Research
Gaithersburg, MD 20899

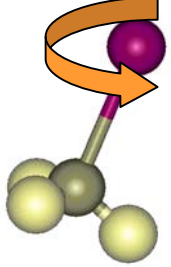
- Introduction
- Bulk and disordered CH_3I dynamics
- Confined CH_3I dynamics
- Conclusions

Introduction

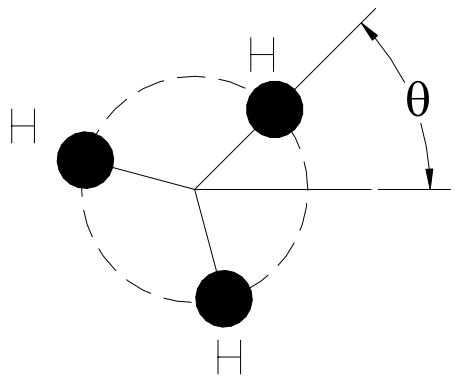
- Confinement induces disorder in adsorbed solids: CH_4 in CPG[1], CH_3I in Geltech[2], H_2 in vycor[3], …
- Adsorbate-surface interactions and modified adsorbate-adsorbate interactions lead to changes in molecular dynamics.
- Sensitivity of rotational tunneling to molecular environment makes rotational tunneling spectroscopy a useful probe of confinement induced disorder.

1. C.Gutt et.al., PRB **59**, 8607 (1999).
2. R.M.Dimeo and D.A.Neumann, PRB **63**, 014301 (2001).
3. D.W.Brown et.al., PRB **59**, 13258 (1999).

Bulk CH_3I Dynamics

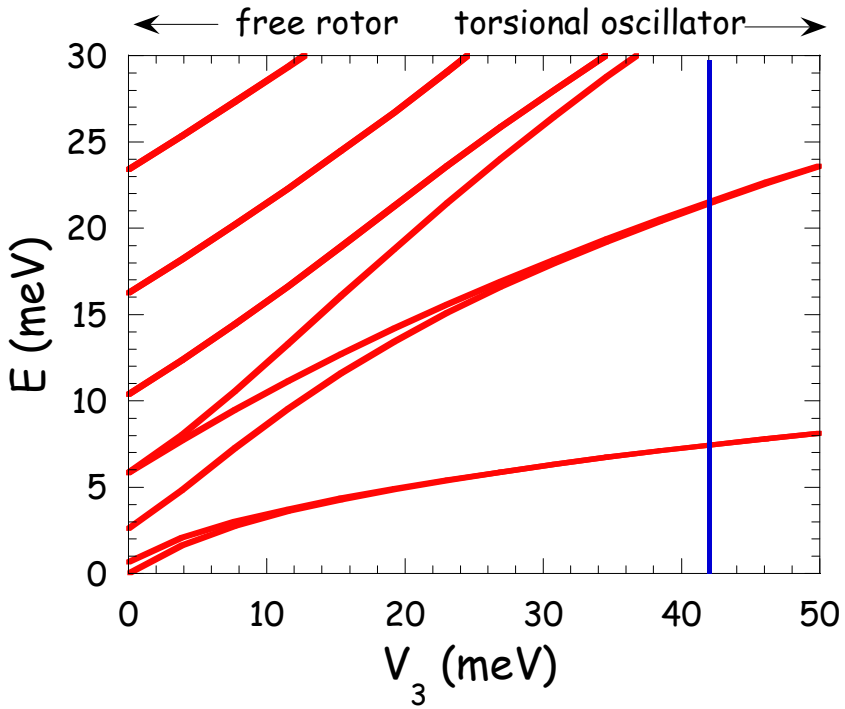


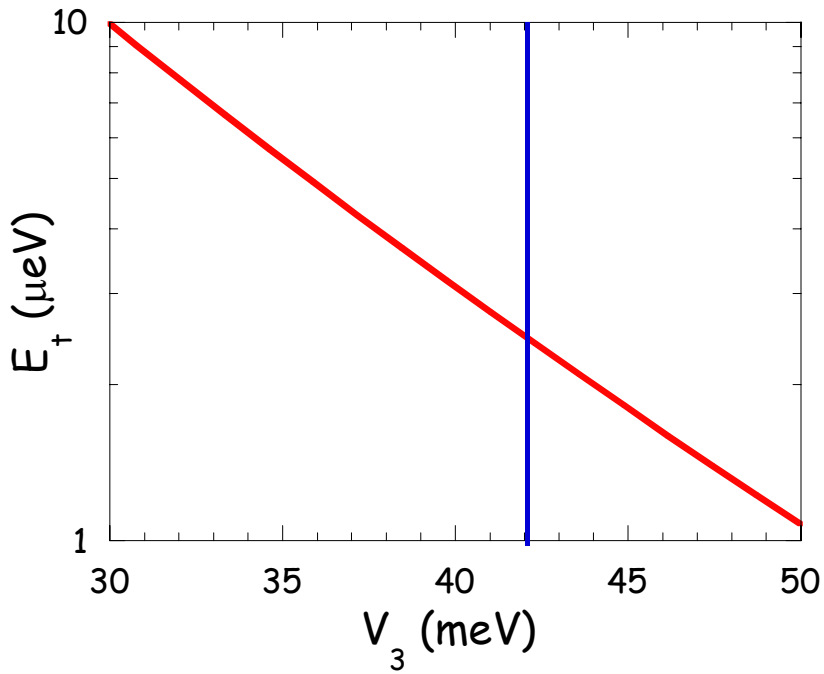
- Quantum rotations, librations, tunneling about main molecular axis
- Three-fold barrier hinders reorientation: $H = -B\frac{d^2}{d\theta^2} + \frac{V_3}{2}(1-\cos 3\theta)$
- θ: angular coordinate for methyl group
- B = 655 μeV, V_3=42 meV in the bulk[1]



1. M.Prager et.al., JCP **86**, 2563 (1986).

Bulk CH_3I Dynamics

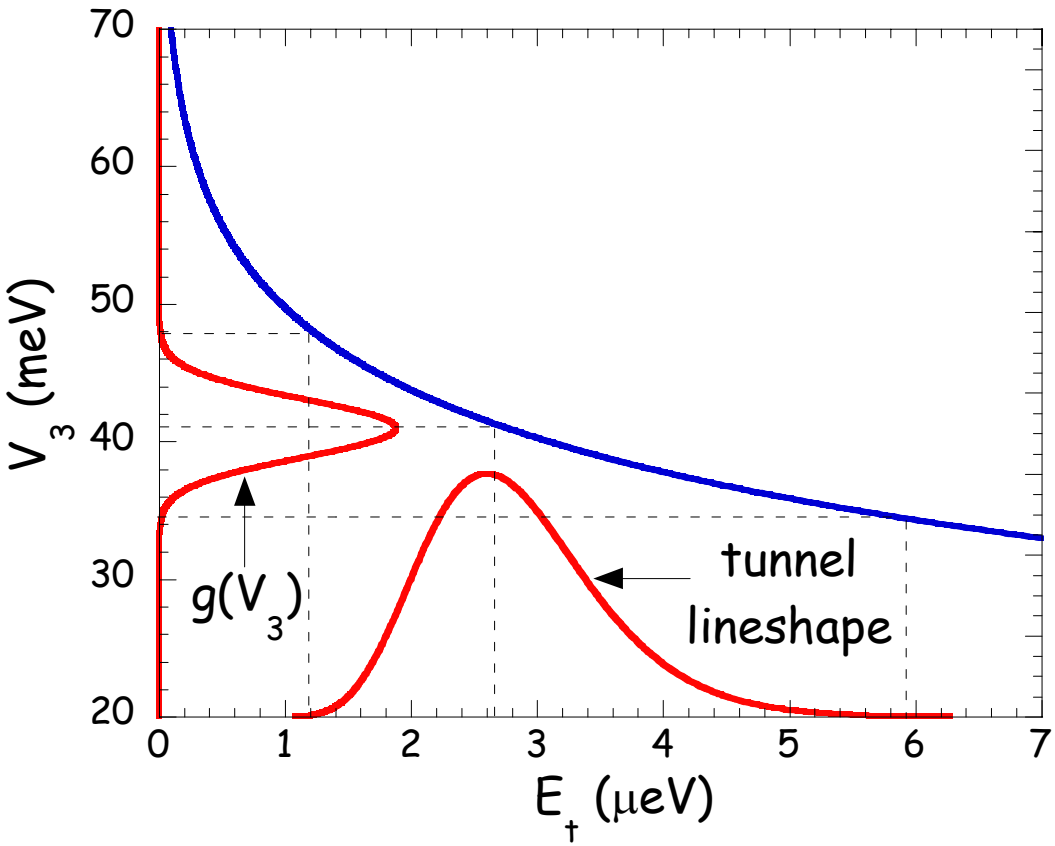




Tunneling energy very sensitive to the barrier height!

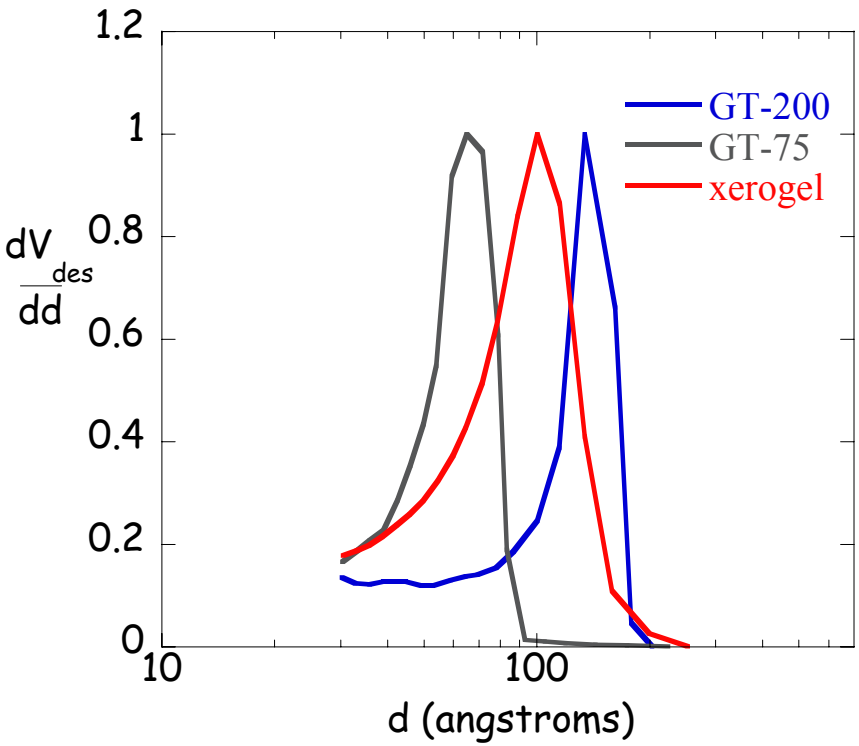
Disordered CH_3I Dynamics

- $g(V_3)$: distribution of barrier heights
- Symmetric distribution of barrier heights leads to asymmetric tunneling lineshape



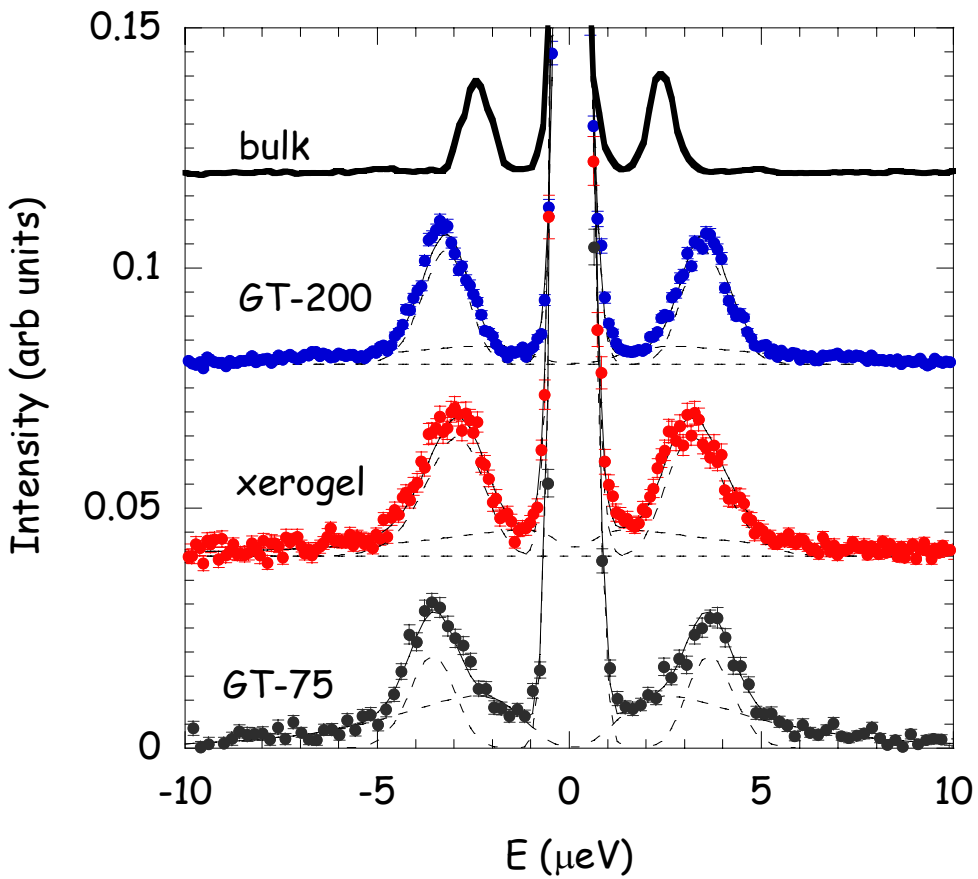
Porous Media

sample	SA (m^2/g)	<d> (nm)	σ_{PSD} (nm)
GT-75	464	6.5	3.0
xerogel	402	10.0	7.6
GT-200	215	14.4	4.5



Confined CH_3I Dynamics

- All measurements performed on HFBS at NIST Center for Neutron Research
- T = 5 K, Q=1.42 A^{-1}
- Two Gaussian components of $g(V_3)$ used in fit
- Narrow: molecules near center of pore
- Broad: closer to pore wall

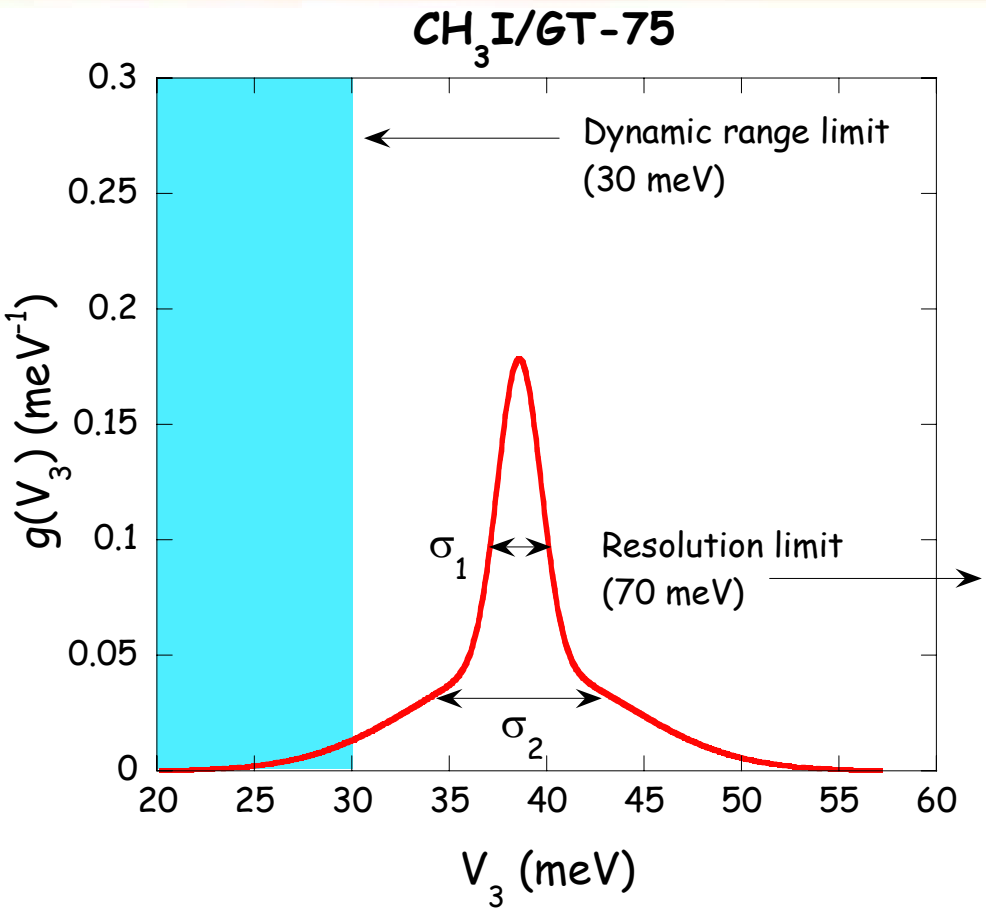


Confined CH_3I Dynamics

- Barrier height distribution used in fits:

$$g(V_3) = \sum_{i=1}^{2} \frac{f_i}{\sqrt{2\pi\sigma_i^2}} \exp\left[-\frac{1}{2}\left(\frac{V_3 - v_{3,i}}{\sigma_i}\right)^2\right]$$

$$f_1 + f_2 = 1$$



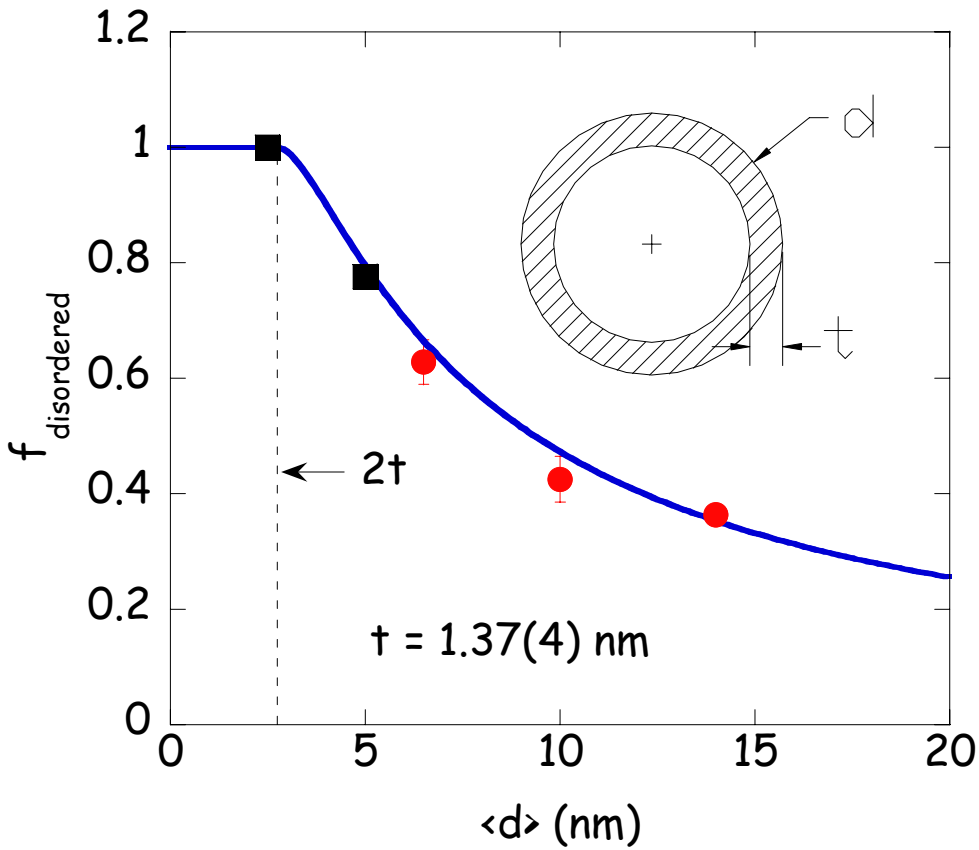
Confined CH_3I Dynamics

- Relative intensities depend on mean pore diameter
- Simple two-component model:

$$f_{\text{disordered}} = \frac{\pi r^2 - \pi(r-t)^2}{\pi r^2}$$

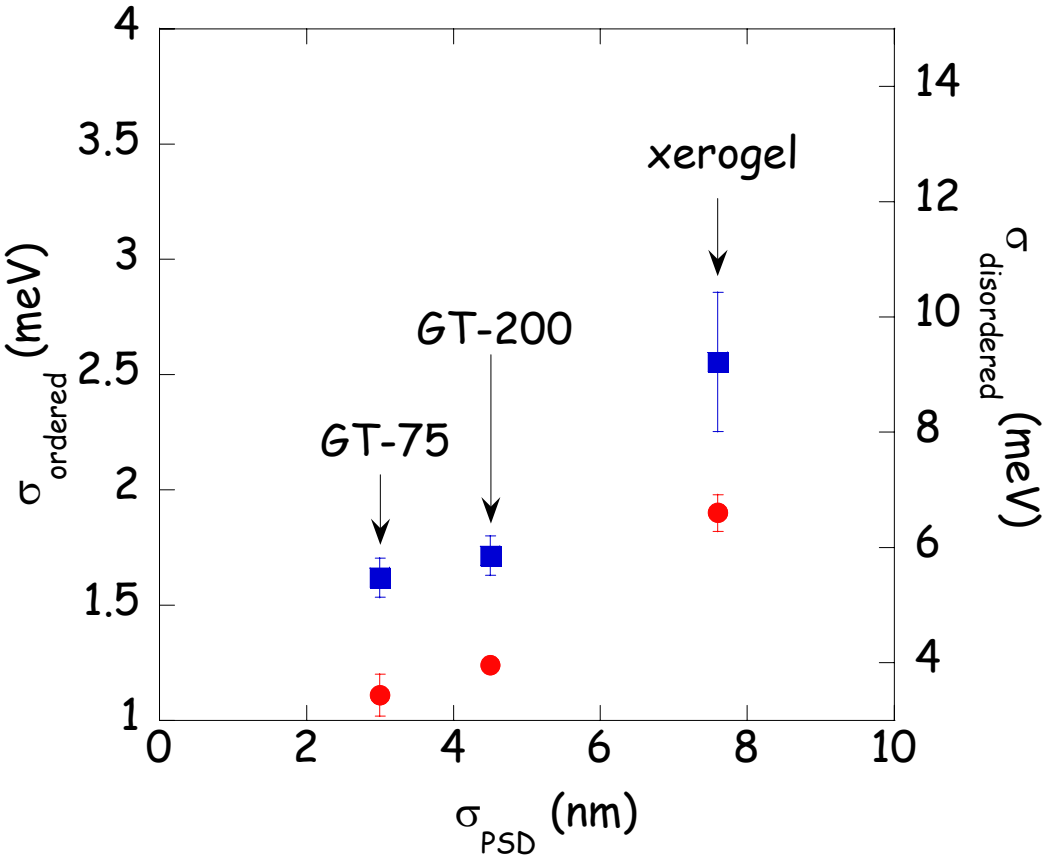
$$= 2\left(\frac{2t}{\langle d \rangle}\right) - \left(\frac{2t}{\langle d \rangle}\right)^2$$

- Thickness of "disordered layer": 1.37(4) nm (~3 molecules)
- Result insensitive to pore size distribution widths.



Confined CH_3I Dynamics

- Widths of each Gaussian component of $g(V_3)$ depends on width of pore size distribution.
- No correlation with the mean pore diameter.



Confined CH_3I Dynamics

- Simple model associates a barrier with a particular pore diameter.

$$V_3 = V_3(d)$$

- Predicts that widths of $g(V_3)$ components correlated with width of pore size distribution…**ok**

$$\sigma_{V_3} = \left|\frac{\partial V_3}{\partial d}\right| \sigma_{PSD}$$

- Predicts that barrier height distribution related to pore size distribution…**no**

$$g(V_3) = P_{pore}(d)\left|\frac{\partial V_3}{\partial d}\right|^{-1}$$

⇒ Barrier height not a simple integral over the pore size distribution.

Conclusions

- Two-component model describes the relative weights of each of the components of $g(V_3)$ based solely on <d>.
- Widths of components of $g(V_3)$ correlated with width of $P_{pore}(d)$
- A single barrier height cannot be associated with a single pore diameter.
- $g(V_3)$ cannot be expressed as a simple integral over the pore size distribution.
- One possibility is adsorbate-surface interactions. CH_3I is polar and porous glass surfaces are hydroxylated.

Acknowledgments

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Inquiries:
dan@nist.gov